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OF ZINC SULFATE, ZINC BASIC
SULFATE, AND THE SYSTEM Zn-S-O

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Thermodynamic Properties of Zinc Sulfate, Zinc Basic Sulfate, and the System Zn-S-O

T. R. Ingraham and H. H. Kellogg

Three anhydrous zinc sulfates have been identified. They are: $ZnSO_4(\alpha)$, stable below $1007^\circ K$; $ZnSO_4(\beta)$, stable above $1007^\circ K$; and $ZnO \cdot 2ZnSO_4$. The decomposition pressure of each sulfate has been measured and the following relations calculated from the results:

$$3ZnSO_4(\alpha) = ZnO \cdot 2ZnSO_4 + SO_3, \quad -R \ln P_{SO_3} \\ = 53,733/T - 45.21 \quad (298^\circ \text{ to } 1007.5^\circ K)$$

$$3ZnSO_4(\beta) = ZnO \cdot 2ZnSO_4 + SO_3, \quad -R \ln P_{SO_3} \\ = 39,281/T - 30.866 \quad (1007.5^\circ \text{ to } 1122^\circ K)$$

$$1/2 (ZnO \cdot 2ZnSO_4) = 3/2 ZnO + SO_3, \quad -R \ln P_{SO_3} \\ = 57,189/T + 3.3 \ln T \\ - 65.629 \quad (298^\circ \text{ to } 1208^\circ K)$$

The measured data have been combined with the known thermodynamic properties of ZnS, ZnO, Zn, SO_2 , and SO_3 to yield univariant and bivariant phase diagrams for the system Zn-S-O. The application of these diagrams to problems of roasting zinc concentrates is discussed.

PRESENT knowledge of the equilibrium chemistry of the system Zn-S-O, so essential to scientific control of zinc-blende roasting, is deficient in several respects. A basic sulfate of zinc has been reported by many investigators, but its composition is in doubt and its thermodynamic properties have not been measured. Our scanty knowledge of the properties of the normal sulfate at roasting temperatures is based on old and inexact studies. A crystal transformation in the normal sulfate, involving a sizable heat effect, has been noted by several investigators but has never been quantified.

The studies reported herein were designed to fill these gaps in knowledge and to make possible a reasonably complete thermodynamic description of the system Zn-S-O at roasting temperatures. The results make possible a far more exact understanding of zinc roasting chemistry than was hitherto possible.

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EXPERIMENTAL

The principal experimental technique employed was the measurement of the total gas pressure developed from decomposition of either $ZnSO_4$ or $ZnO \cdot 2ZnSO_4$ in a closed system. The apparatus employed was essentially the same as that described by Warner and Ingraham¹ and Flengas and Ingraham.² The unusual feature is a flexible Pyrex bellows used to separate the reaction gas mixture (SO_3 , SO_2 , and O_2) from the mercury in the manometer and thus prevent corrosion of the mercury by SO_3 . The bellows operates without evidence of hysteresis and, barring accidents, may be used for several months. The response of the bellows varies from manometer to manometer, but is generally of the order of 0.6-cm displacement for a 1-cm change in pressure. The response for all manometers has been linear over the range 0 to 1 atm. To prevent condensation and polymerization of sulfur trioxide, the bellows-manometer was maintained at $100.0^\circ \pm 0.5^\circ C$ by a circulating bath of silicone oil. The connecting tubing between the manometer and the furnace was maintained at $100.0^\circ \pm 0.2^\circ C$ also, with a stirred air bath. The open end of the manometer was connected with a chamber which was maintained at a known pressure. The pressure could be varied so that readings of the height of the mercury column, measured with a cathetometer, could be made with both rising and falling mercury column. By using the average of the readings, any error due to sticking of the mercury column was minimized.

The sample was placed in a 2-in.-long platinum boat formed into the shape of a half-cylinder. The sample was prepared as a fine powder and pressed against the inner wall of the platinum boat. A silica thermocouple well, covered with a platinum sleeve, was placed lengthwise along the center of the boat. The temperature of the sample was read on a calibrated Pt-10 pct Rh thermocouple. The temperature profile of the furnace was constant within $\pm 0.2^\circ C$ over the length of furnace occupied by the sample.

The horizontal furnace used to contain the sample and the quartz reaction tube was electrically heated, with the control thermocouple placed 1/4 in. from the windings. A Brown Pyro-O-Vane temperature controller with a 3-sec response time was used to maintain the furnace temperature.

Before beginning a run, the apparatus, including the bellows manometer, was thoroughly washed *in situ* with acid and distilled water to remove any

Table I(a). Summary of Results for Decomposition of ZnSO₄ to ZnO·2ZnSO₄

Point No.	°K	10 ⁴ /°K	P _{tot} , Atm	P _{SO₄} , Atm	-R ln P _{SO₄}
1	952.3	10.501	0.02209	0.003196	11.418
2	954.9	10.472	0.02588	0.003886	11.030
3	957.2	10.447	0.02741	0.004116	10.915
4	960.4	10.412	0.03047	0.004622	10.685
5	966.5	10.347	0.03508	0.005305	10.411
6	970.6	10.303	0.04136	0.006415	10.034
7	976.4	10.242	0.04371	0.006558	9.990
8	980.7	10.197	0.04997	0.007592	9.699
9	988.3	10.118	0.06289	0.009747	9.202
10	990.1	10.100	0.06660	0.01039	9.075
11	997.4	10.026	0.08622	0.01393	8.493
12	1008.1	9.920	0.10646	0.01699	8.098
13	1012.9	9.873	0.11691	0.01856	7.922
14	1015.1	9.851	0.12000	0.01889	7.887
15	1015.7	9.845	0.12405	0.01968	7.806
16	1031.7	9.693	0.16760	0.02612	7.243
17	1035.8	9.654	0.19070	0.03021	6.954
18	1045.0	9.569	0.21150	0.03236	6.818
19	1055.0	9.479	0.27284	0.04256	6.273
20	1058.7	9.446	0.29222	0.04548	6.141
21	1066.2	9.379	0.31779	0.04818	6.027
22	1068.6	9.358	0.33429	0.05075	5.923
23	1084.1	9.224	0.45082	0.06836	5.332
24	1089.2	9.181	0.48159	0.07213	5.225
25	1115.2	8.967	0.75694	0.11207	4.349
26	1122.0	8.913	0.83253	0.12196	4.181

Table I(b). Summary of Results for Decomposition of ZnO·2ZnSO₄ to ZnO

Point No.	°K	10 ⁴ /°K	P _{tot} , Atm	P _{SO₄} , Atm	-R ln P _{SO₄}
1	1085.7	9.211	0.08154	0.005919	10.193
2	1094.0	9.141	0.10105	0.007525	9.716
3	1095.9	9.125	0.10352	0.007668	9.679
4	1111.8	8.994	0.14829	0.01131	8.907
5	1123.4	8.902	0.18333	0.01401	8.481
6	1140.0	8.772	0.26085	0.02049	7.726
7	1152.0	8.681	0.33323	0.02665	7.203
8	1167.5	8.565	0.43568	0.03501	6.661
9	1180.2	8.473	0.55413	0.04521	6.153
10	1192.3	8.387	0.69396	0.05746	5.677
11	1201.7	8.322	0.79006	0.06495	5.433
12	1207.9	8.279	0.88499	0.07335	5.192

traces of sample or products remaining from the previous run. The apparatus was then dried by sealing and evacuating for 10 hr at operating temperature. After cooling, the furnace tube was opened, a previously dried sample introduced, and then the apparatus was sealed and evacuated with a rotary pump for an additional period of several hours. In the final period of 1 hr before the apparatus was isolated from the pump, the temperature of the sample was increased slowly until incipient decomposition had begun. The required temperature for this purpose was determined from the pressure-temperature data of a preliminary run. After the apparatus had been sealed, the temperature was increased to a prechosen value, and measurements of the pressure were made at 1/2-hr intervals. When it was noted that the pressure had been unchanged for periods between 3 hr and overnight, the temperature was increased to obtain the next higher equilibrium temperature-pressure relationship. The equilibrium was readily reversible if the system was not displaced more than a few degrees from its equilibrium temperature. If the displacement was large (equivalent to half an atmosphere total pressure), periods up to 10 hr were

required for re-establishment of equilibrium. This lack of ready reversibility has been attributed by Alcock³ to the low permeability of sulfate coatings on the oxide.

To determine whether the results were affected by thermal diffusion, as suggested by Warner,⁴ an all-pyrex centrifugal circulation pump was installed in the system in a bypass between the bellows of the manometer and the hot furnace tube. The circulating pump was not used continuously, but it was observed that after it had been started there was a short period of thermal instability, following which the system settled to its original pressure readings at the set temperature. This demonstrated that the effects of thermal diffusion were not detectable in the system.

Zinc sulfate* and zinc oxide used in the exper-

*This was prepared from ZnSO₄·7H₂O by dehydration for 24 hr at 380°C.

iments were reagent grade and not further purified. The basic sulfate, ZnO·2ZnSO₄, was prepared by mixing stoichiometric quantities of ZnO and ZnSO₄ in a pebble mill for 24 hr. The mixture was then pelletized and heat-treated at 700°C for 24 hr. X-ray diffraction patterns of the product indicated the presence of traces of ZnO, but no evidence of ZnSO₄.

In addition to the decomposition-pressure measurements a number of auxiliary experiments involving differential thermal analysis, thermogravimetric analysis, and X-ray diffraction were made. These are described at appropriate places in the Discussion section.

RESULTS AND DISCUSSION

Composition of Basic Zinc Sulfate. The existence of a basic sulfate of zinc has been reported by many previous investigators but opinion has been divided regarding the composition of this substance. The most frequently reported compositions are 2ZnO·3ZnSO₄^{5,6} and ZnO·2ZnSO₄.^{7,8} In a recent study, Flood and Boye⁸ assign the latter composition and claim to have prepared the compound by mixing stoichiometric amounts of ZnO and ZnSO₄ and heat-treating the mixed pellets at 700°C for 24 hr. After three repetitions of this process, with intermediate grinding of the pellets, they obtained X-ray patterns of the product which were free from diffraction lines for ZnO and ZnSO₄. Hoschek,⁵ on the other hand, assigns the former composition, based on thermogravimetric analysis of the decomposition of ZnSO₄.

Our experiments with both thermogravimetric and X-ray analysis support the composition ZnO·2ZnSO₄. A sample of ZnSO₄ subjected to thermogravimetric study* lost weight in two distinct stages: 59.5 mg

*The heating rate was 3°C per min over the temperature range 500°-1000°C. The sample weight was continuously and automatically recorded.

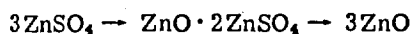
loss between 650° and 835°C, and 120.5 mg be-

Table II. X-ray Diffraction Data for ZnO · 2ZnSO₄

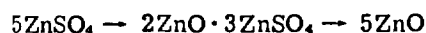
Diffractometer (Columbia)		114.6-Mm Camera (Mines Branch)	
<i>d</i> , Å	<i>l/l</i>	<i>d</i> , Å	<i>l/l</i>
—	—	10.67	40
—	—	6.96	50
—	—	6.49	60
—	—	4.65	40
4.67	20	3.94	50
3.94	55	3.90	50
3.91	60	3.67	80
3.68	95	3.48	60
3.48	80	3.34	80
3.34	85	3.23	50
3.23	45	3.01	30
3.01	35	2.97	100
2.97	95	2.544	60
2.54	70	2.509	70
2.51	75	2.470	100
2.47	100	2.410	80
2.41	80	2.104	50
2.11	30		

*Filtered CuK radiation used with diffractometer; filtered CoK radiation used with camera. Several weak lines (intensities less than 20 pct) have been omitted from the table, as well as lines for $2\theta > 44^\circ$. The intensity at $d = 2.47\text{Å}$ may be slightly reinforced by the presence of a trace of ZnO in the sample.

tween 835° and 975°C . The ratio of weight loss for the two stages, $59.5/120.5 = 1/2.03$, is almost exactly in conformity with the scheme



from which weight losses in the ratio 1/2 are expected. Decomposition by the scheme



would result in weight losses with a ratio of 2/3 or 1/1.5. Our X-ray investigations confirm the findings of Flood and Boye.

None of our data suggests the possibility of two different basic sulfates. It is most likely that all investigators have studied the same compound but reported different formulas as a result of the difficulty of distinguishing the small difference in composition between $\text{ZnO} \cdot 2\text{ZnSO}_4$ and $2\text{ZnO} \cdot 3\text{ZnSO}_4$. Support for this view comes from the fact that Hoschek⁹ reports an X-ray powder pattern for his alleged $2\text{ZnO} \cdot 3\text{ZnSO}_4$ which agrees with our pattern for $\text{ZnO} \cdot 2\text{ZnSO}_4$ within experimental error. The major X-ray lines and relative intensities for $\text{ZnO} \cdot 2\text{ZnSO}_4$ are given in Table II.

Decomposition Pressure Results. Equilibrium pressure measurements for decomposition of ZnSO_4 and $\text{ZnO} \cdot 2\text{ZnSO}_4$ are given in Tables I(a) and I(b). For each experimental point the equilibrium partial pressure of SO_3 has been calculated from knowledge of the equilibrium constant* for the reaction

*We have used the data of Wagman and Evans⁽⁷⁾ to calculate the equilibrium constant for this reaction and we have expressed the results by the empirical equation

$$\log K (\text{atm}) = 8.8557 - 5465.5/T - 1.21572 \log_{10} T$$

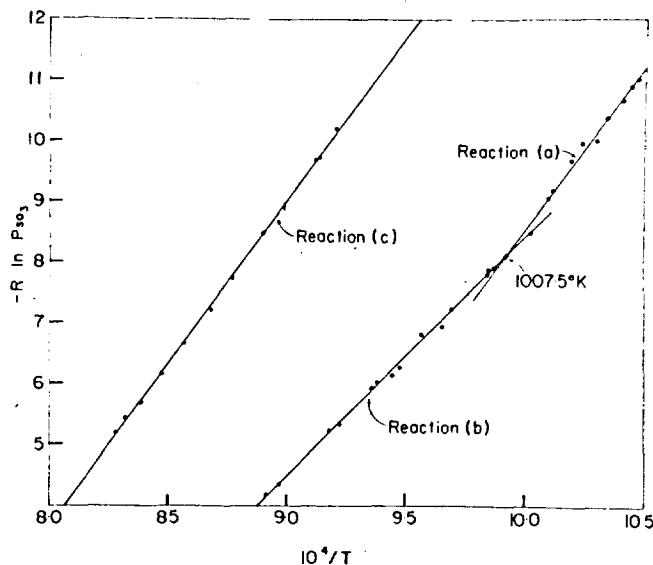
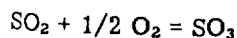


Fig. 1—Relation between temperature and the partial pressure of SO_3 calculated from total pressure measurements. Reactions (a), (b), and (c) refer to reaction equations in the text.

and from the knowledge that the gas phase must contain twice as much SO_2 as O_2 .*

*Warner⁴ has pointed out that thermal diffusion within the experimental apparatus could destroy the validity of this $P_{\text{SO}_3} - P_{\text{O}_2}$ relation in the hot zone. His estimate of the possible magnitude of this error in sulfate decomposition is far too large, however, as a result of the presence of an unsuspected side reaction in his study of the decomposition of cobalt sulfate.¹⁰

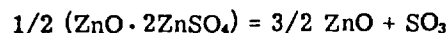
$$P_{\text{SO}_2} = 2P_{\text{O}_2}$$

Table I gives the results of these calculations.

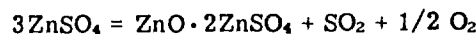
Fig. 1 displays the relations between $-R \ln P_{\text{SO}_3}$ and $10^4/T$ for all of the pressure measurements. The fact that considerably higher temperatures are required to decompose $\text{ZnO} \cdot 2\text{ZnSO}_4$ than to decompose ZnSO_4 is illustrated by the considerable displacement between the two curves. A sample of the material from partly decomposed ZnSO_4 shows X-ray lines for ZnSO_4 and $\text{ZnO} \cdot 2\text{ZnSO}_4$; a sample from partly decomposed $\text{ZnO} \cdot 2\text{ZnSO}_4$ shows X-ray lines for $\text{ZnO} \cdot 2\text{ZnSO}_4$ and ZnO . It follows that the reactions corresponding to these decompositions are:



and



Other measurements of zinc sulfate equilibria which can be compared with ours are those of Wöhler and Plüddemann,¹¹ who studied the thermal decomposition of ZnSO_4 , and Flood and Boye,⁸ who made cell measurements for the reaction



in the temperature range 780° to 880°K . The re-

sults of Wöhler and Plüddemann are badly scattered and yield pressures which are 30 to 70 pct lower than ours. Their method of separating the reaction gas from the mercury manometer was ingenious but of doubtful accuracy* and the dis-

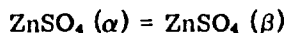
*An air-filled chamber was connected directly to the manometer and to the reaction system via a stopcock. The air pressure in the chamber was adjusted to be lower than the pressure in the reaction system. The stopcock was then opened momentarily and the deflection of the manometer noted. The process was then repeated, with increasing air pressure in the chamber, until no deflection of the manometer was noted.

cordance of their results and ours probably result from errors in this device. The results of Flood and Boye, obtained by a novel fused-salt electro-motive force measurement, are for a temperature range about 200°C lower than ours. If their measurements are converted to values of P_{SO_3} and compared with our results extrapolated into their temperature range, their values of P_{SO_3} are about 30 pct lower than ours. The discrepancy here may result from failure of the fused-salt melt to reach equilibrium with solid $ZnSO_4$ and $ZnO \cdot 2ZnSO_4$.*

*Flood and Boye mention that the melts are highly viscous and show a strong tendency for supercooling.

An additional reason to question the accuracy of their measurements lies in the fact that extrapolation of their results to room temperature yields values of ΔH_f° and S° for $ZnSO_4$ which are outside of accepted limits for these properties.

Crystal Transformation in $ZnSO_4$. Of particular interest is the abrupt change in slope in Fig. 1 for the pressure-temperature graph of $ZnSO_4$ (c) at 1007°K. DTA measurements on $ZnSO_4$ consistently show a sharp and reversible endothermic peak at about this temperature, indicative of a crystal transformation. Indeed, as long ago as 1910, Friedrich and Blicke¹² reported such a transformation at 1013°K, and it has been reported many times since then. The change in slope of the line on Fig. 1 on passing through the transformation temperature should yield three times the enthalpy of transformation of $ZnSO_4$ (c). From this we estimate:



$$\Delta H^\circ = 4820 \text{ cal at } 1007.5^\circ\text{K}$$

Changes in crystal structure on heating are common for the metal sulfates, but the large magnitude of the enthalpy at first led us to doubt the validity of the measurements. Reference to the literature, however, supports the possibility of large heats of transformation for complex salts.*

*For example, Kubaschewski and Evans⁽¹³⁾ report the following transformation enthalpies: $BaCO_3$, 4.5 kcal; Li_2SO_4 , 6.8 kcal; K_2SO_4 , 2.14 kcal; Mn_2O_3 , 5.0 kcal; $PbSO_4$, 4.1 kcal.

An independent estimate of the heat of transformation of $ZnSO_4$ was obtained by performing a DTA measurement in which the "reference substance" was K_2SO_4 (this salt undergoes a transformation at 583°C with an enthalpy of 2140 cal per mole) and $ZnSO_4$ was the "unknown." The DTA

peaks for transformation of both K_2SO_4 and $ZnSO_4$ are thus produced in opposed fashion on the same graph. The peaks were recorded both on heating and cooling and the area under each peak was measured (average values on heating and cooling were used). From a knowledge of the number of moles of $ZnSO_4$ and K_2SO_4 present in the DTA apparatus it was possible to calculate the "peak area" per mole for each substance. The relative enthalpies were then estimated from the relation:

$$\frac{\text{peak area per mole } ZnSO_4}{\text{peak area per mole } K_2SO_4} = 2.138$$

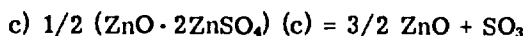
$$= \frac{\Delta H^\circ_{ZnSO_4} (\alpha \rightarrow \beta)}{\Delta H^\circ_{K_2SO_4} (\alpha \rightarrow \beta)}$$

$$\Delta H^\circ_{ZnSO_4} (\alpha \rightarrow \beta) = 2.138 \times 2140 = 4575 \text{ cal/mole}$$

The agreement between this measurement and the value found from the change in slope on Fig. 1 is evidence of the correctness of the interpretation.

The significant difference in slope for the decomposition pressures of the α and β forms of $ZnSO_4$ explain the failure of extrapolated room temperature properties of $ZnSO_4$ (α) to yield correct values of decomposition pressures above 1007°K (734°C).

Correlation of Data at 298.15°K. The reactions corresponding to the pressures shown on Fig. 1 are:



To extrapolate the measurements to 298°K with accuracy would require a knowledge of the heat capacity for each substance as a function of temperature. Such data are lacking for the basic sulfate and for $ZnSO_4$ (β). We believe, however, that even a crude correlation of the data for reactions (a) and (c) at 298°K is justified to check the reasonableness of the resulting values for ΔH° and S° for the normal and basic sulfates. The following assumptions and arguments underlie our approximate extrapolation.

1) The average value of ΔC_p for reaction (a) is taken as zero for the range 298° to 1000°K. Our reasons for this choice follow. If the heat capacity of $ZnO \cdot 2ZnSO_4$ were equal to the sum of the heat capacities of $ZnO + 2ZnSO_4$, then reaction (a) would have a small negative value of ΔC_p (-1.56 cal per °C per mole at 298°K); as will be established later, however, the entropy of formation of $ZnO \cdot 2ZnSO_4$ from ZnO and $2ZnSO_4$ has a small positive value and we believe it likely that the heat capacity of the basic sulfate is also slightly larger than the sum of the heat capacities of $ZnO + 2ZnSO_4$. Therefore, in the absence of more exact data, we estimate $\Delta C_p = 0$ for reaction (a).

2) ΔC_p for reaction (c) is assigned the value -3.3 cal per °C per mole, as an average value for the range 298° to 1000°K. This value is chosen to

Table III. Equilibrium Constants for Basic Reactions in Zn-S-O System*

Reaction	Log K				
	900°K	1000°K	1100°K	1200°K	1300°K
(a) $3ZnSO_4(\alpha) = ZnO \cdot 2ZnSO_4 + SO_2$	-3.1675	-1.8627	—	—	—
(b) $3ZnSO_4(\beta) = ZnO \cdot 2ZnSO_4 + SO_2$	—	—	-1.0586	-0.4083	0.1420
(c) $1/2 (ZnO \cdot 2ZnSO_4) = 3/2 ZnO + SO_2$	-4.4501	-3.1374	-2.0699	-1.1857	-0.4423
(e) $Zn(l, g) + 1/2 S_2 = ZnS$	10.3436	8.7779	7.5005	6.3539	5.0597
(f) $Zn(l, g) + 1/2 O_2 = ZnO$	14.9219	12.8724	11.1956	9.7163	8.1535
(g) $1/2 S_2 + O_2 = SO_2$	17.1960	15.0940	13.3760	11.9430	10.7310
(h) $1/2 O_2 + SO_2 = SO_3$	0.8100	0.2570	-0.1900	-0.5590	-0.8660

*Data for reactions (a), (b), and (c) calculated from correlation equations for experimental work in this paper. Data for reaction (e) calculated from values given by Kelley, (12,13) Stull and Sinke, (14) and Kubaschewski and Evans. (15) Reaction (f) based on Coughlin. (16) Reactions (g) and (h) from Evans and Wagman. (17) Accuracy of all values is no better than the third decimal, but fourth decimal is retained in order to improve the internal consistency of the values in Tables IV and V.

Table IV. Stable Univariant Equilibria in the System Zn-S-O*

Reaction	Log K				
	900°K	1000°K	1100°K	1200°K	1300°K
A $ZnS + 11ZnSO_4(\alpha) = 4(ZnO \cdot 2ZnSO_4) + 4SO_2$	10.6969	13.6792	—	—	—
B $ZnS + 11ZnSO_4(\beta) = 4(ZnO \cdot 2ZnSO_4) + 4SO_2$	—	—	15.1395	16.2758	17.2383
C $2ZnS + 3(ZnO \cdot 2ZnSO_4) = 11ZnO + 8SO_2$	11.9880	18.0106	22.8628	26.8506	30.1918
D $ZnS + 2ZnO = 3Zn(l) + SO_2$	-22.9914	-19.4287	-16.5157	—	—
E $ZnS + 2ZnO = 3Zn(g) + SO_2$	—	—	—	-13.8435	-10.6357

*Calculated from the data of Table III.

be consistent with the zero value of ΔC_p assigned to reaction (a).^{*} Further evidence that reaction (c) has

^{*}The data of Kelley (12) may be used to calculate the following average values of C_p for the range 298° to 1000°K: ZnO = 11.7; SO₂ = 16.9; ZnSO₄(α) = 30.8. If the latter two of these values are used in reaction (a) with the assigned value of $(\Delta C_p)_a = 0$, there results: $C_p = 75.5$ for the basic sulfate. Therefore, for reaction (c)

$$\Delta C_p = 3/2 \cdot 11.7 + 16.9 - \frac{75.5}{2} = -3.3$$

a negative value of ΔC_p comes from the fact that log $P_{SO_2} - 1/T$ plot of the data exhibits a slight curvature indicative of such a value.

Corresponding to these assumptions, for reaction (a) we write:

$$(\Delta C_p)_a = 0$$

$$\frac{\Delta F^\circ}{T} = -R \ln P_{SO_2} = \frac{\Delta H^\circ}{T} - \Delta S^\circ$$

The values of ΔH° and ΔS° were determined by "least squares" analysis of points 2 to 12 of Table I(a).^{*} The resulting constants are:

^{*}Point 1, at the lowest temperature, was omitted from the statistical analysis because it deviates furthest from the line and is subject to the largest uncertainty in pressure measurement.

$$-R \ln P_{SO_2} = 53,733/T - 45.21 \quad [\text{reaction (a)}]$$

$$\Delta H_{298}^\circ = 53,733$$

$$\Delta S_{298}^\circ = 45.21$$

For reaction (c):

$$(\Delta C_p)_c = -3.3$$

$$\Sigma = -R \ln P_{SO_2} - 3.3 \ln T$$

The value of Σ was calculated for each experimental point of Table I(b). A "least squares" analysis leads to the relations:

$$\Sigma = 57,189/T - 65.629$$

$$\frac{\Delta F^\circ}{T} = -R \ln P_{SO_2} = 57,189/T + 3.3 \ln T - 65.629$$

[reaction (c)]

$$\Delta H_{298}^\circ = 56,205$$

$$\Delta S_{298}^\circ = 43.527$$

There is no need to extrapolate reaction (b) to 298°K, but for purposes of obtaining smoothed values for this reaction and to extrapolate to higher temperatures, the following correlation is used:

$$(\Delta C_p)_b = 0$$

$$\frac{\Delta F^\circ}{T} = -R \ln P_{SO_2} = 39,281/T - 30.866$$

[reaction (b)]

The value of the constants in this equation were determined by "least squares" analysis of points 13 to 26 in Table I(a).

If the values of ΔH_{298}° and ΔS_{298}° for reaction (c) are combined with accepted values^{*} for the enthalpy and

^{*}For ΔH_f° we use the values of Coughlin, (18) -83,250 for ZnO and -94,470 for SO₂; for S_{298}° we use the data of Kelley, (12) 10.43 for ZnO and 61.2 for SO₂.

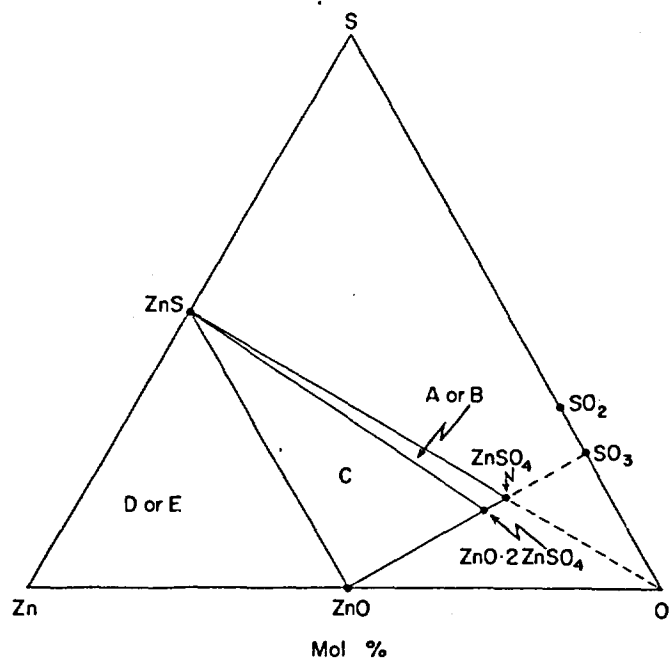


Fig. 2—Stable univariant equilibria in the system Zn-S-O. A, B, C, D, and E refer to equilibrium reactions given in Table IV.

entropy of ZnO and SO₃, there results for ZnO · 2ZnSO₄ (c):

$$\Delta H_{f298}^{\circ} = -551,100 \text{ cal}$$

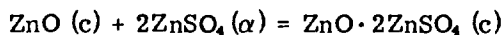
$$\Delta S_{298}^{\circ} = 66.64$$

These values for the basic sulfate combined with ΔH_{298}° and ΔS_{298}° for reaction (a) and the known enthalpy and entropy of SO₃ yield, for ZnSO₄ (α):

$$\Delta H_{f298}^{\circ} = -233,100$$

$$S_{298}^{\circ} = 27.54$$

Finally, combination of the results for the basic sulfate and ZnSO₄ (α) yields [reaction (d)]:



$$\Delta H_{298}^{\circ} = -1650$$

$$\Delta S_{298}^{\circ} = +1.13$$

All of these calculated room-temperature properties are consistent with our present knowledge. For example: the heat of formation of ZnSO₄ (α) is given¹⁷ as -233,880 with an uncertainty of about ±1000 cal. Kelley's most recent estimate of the entropy of ZnSO₄ (α) is 27.0 ± 1.¹⁸ Flood and Boye⁸ have made a calorimetric determination of ΔH_{298}° for reaction (d) and report the value -1700 ± 900 cal. Though our room-temperature values are probably uncertain to ±1000 cal in ΔH° and ±1.0 eu in ΔS° as a result of the uncertainty in the extrapolation, we believe that the internal consistency of the correlation argues strongly in favor of the validity of the measurements and interpretation.

Thermodynamic Phase Diagram for Zn-S-O System. The availability of reliable high-temperature equilibrium data for the various zinc sulfates

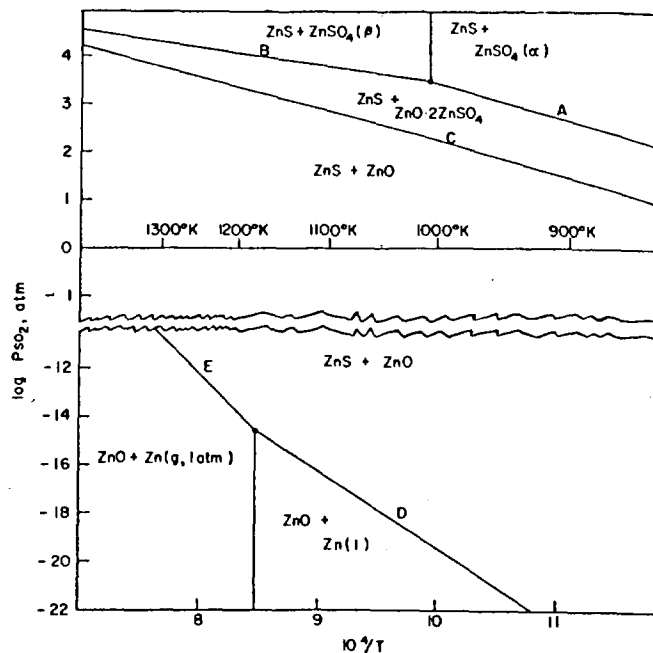


Fig. 3—Stable univariant equilibria in the system Zn-S-O. A, B, C, D, and E refer to equilibrium reactions given in Table IV. Areas are regions of stability of two condensed phases as marked.

makes possible the construction of thermodynamic phase diagrams for the ternary system, showing the stable univariant and bivariant equilibrium relations. The construction and use of such diagrams has been discussed by Kellogg and Basu¹⁸ and applied to the system Pb-S-O. It is sufficient here to present the results and discuss specific features of the system Zn-S-O.

In addition to the equilibrium constants for reactions (a), (b), and (c), measured in this study, it is necessary to have values for the equilibrium constants for formation of ZnO, ZnS, SO₂, and SO₃ in order to construct the diagrams. All of these are known with sufficient accuracy and the values are reported in Table III at 100 deg intervals between 900° and 1300°K. Sources of the data are given in the footnote to that table.

Combination of the data of Table III makes it possible to decide which of the several possible univariant equilibria are stable and which metastable, and to calculate the values of the equilibrium constant for each of these. Table IV lists values for the stable univariant equilibria. Fig. 2 shows the stable univariant equilibrium triangles on a composition plot, and Fig. 3 shows the univariant equilibria plotted as log P_{SO₂} vs 10⁴/T.

It is interesting to note that, in the temperature interval 900° to 1300°K, only one true invariant point is found: that resulting from the crystal transformation in ZnSO₄ at 1007°K. The other apparent invariant point at 1181°K results from the arbitrary selection of 1 atm pressure to divide the fields of stability of liquid and gaseous zinc. Another peculiarity of the Zn-S-O system is that the univariant equilibria exhibit SO₂ pressures which

Table V. Stable Bivariant Equilibria in the System Zn-S-O*

	Log K				
	900°K	1000°K	1100°K	1200°K	1300°K
1 $ZnS + 2O_2 = ZnSO_4 (\alpha, \beta)$	26.6069	22.1580	18.6139	15.6730	13.2063
2 $3ZnSO_4 (\alpha, \beta) = ZnO \cdot 2ZnSO_4 + SO_2 + 1/2 O_2$	-3.9775	-2.1197	-0.8686	0.1507	1.0080
3 $3ZnS + 11/2 O_2 = ZnO \cdot 2ZnSO_4 + SO_2$	75.8431	64.3544	54.9731	47.1697	40.6271
4 $1/2(ZnO \cdot 2ZnSO_4) = 3/2 ZnO + SO_2 + 1/2 O_2$	-5.2601	-3.3944	-1.8799	-0.6267	0.4237
5 $ZnS + 3/2 O_2 = ZnO + SO_2$	21.7743	19.1885	17.0711	15.3054	13.8248
6 $Zn (l, g) + SO_2 = ZnS + O_2$	-6.8524	-6.3161	-5.8755	-5.5891	-5.6713
7 $2Zn (l, g) + O_2 = 2ZnO$	29.8438	25.7448	22.3912	19.4326	16.3070

*Calculated from the data of Table III.

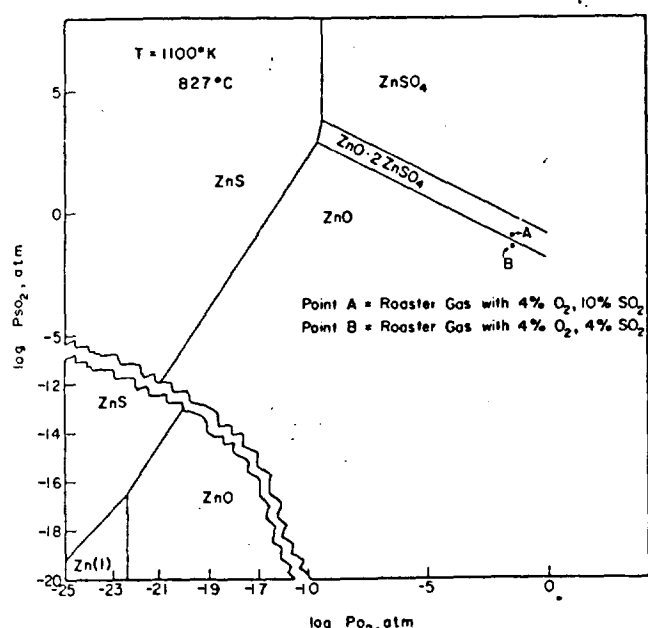


Fig. 4—Stable bivariant equilibria in the system Zn-S-O at 1100°K. Areas are regions of stability of one condensed phase as marked.

are either too high (A, B, C) or too low (D, E) for direct measurement. This contrasts with the Pb-S-O system where most of the univariant equilibria have pressures in the measurable range.

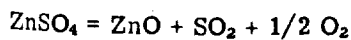
Further combinations of the data of Table III lead to calculated values for the bivariant equilibria. The stable bivariant equilibria are given in Table V and are plotted as $\log P_{SO_2}$ vs $\log P_{O_2}$ for the single temperature of 1100°K in Fig. 4.

The equilibrium diagrams illustrate several significant facts about the Zn-S-O system.

1) Unlike the Pb-S-O system, the field of stability of zinc metal is bounded by extremely low values of P_{O_2} and P_{SO_2} . Thus roast-reduction type of reactions, common in lead and copper metallurgy, are ruled out in zinc metallurgy.

2) The sulfates of zinc are much less stable than the sulfates of lead.

3) The equilibrium decomposition of $ZnSO_4$ has often been erroneously written as



The existence of the basic sulfate, now firmly established, makes a stable equilibrium between

ZnO and $ZnSO_4$ an impossibility. Rather, the sulfate must decompose in two stages, represented by reactions 2 and 4 of Table V.

4) A roaster operated under conditions for production of a small amount of sulfate in the calcine should yield the basic sulfate, not the normal sulfate. It would be most interesting to examine such products by X-ray diffraction to establish this point.

5) If a roaster is operated close to equilibrium, then Fig. 4, and similar figures for other temperatures, can be used to predict the nature of the calcine in roasting of sphalerite. For example, Fig. 4 shows that a roaster operated at 1100°K (827°C), with 4 pct mole O_2 and 10 pct mole SO_2 in the roaster gas, will produce a calcine of basic sulfate. A higher roaster temperature, or a gas leaner in SO_2 and O_2 , is required to produce a calcine of ZnO .

We hope that those concerned with the metallurgy of zinc will find many other uses of the data presented herein.

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The authors are pleased to acknowledge the following contributions by members of the Mines Branch Staff: J. F. Rowland, X-ray data; P. Hernandez, construction of bellows-manometer; R. A. Charlebois, operation of equipment; R. H. Lake, differential thermal analysis; P. Marier, thermogravimetric analysis; and M. E. V. Plummer, preparation of $ZnO \cdot 2ZnSO_4$ sample.

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¹¹K. K. Kelley: *U. S. Bur. Mines, Bull.*, no. 584, 1960.

¹²J. P. Coughlin: *U. S. Bur. Mines, Bull.* no. 542, 1954.

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¹⁴F. Rossini et al.: *Nat. Bur. Std. (U.S.) Circ.* no. 500, 1952.

¹⁵H. H. Kellogg and S. K. Basu: *Trans. Met. Soc. AIME*, 1960, vol. 218, p. 70.

¹⁶D. Stull and G. Sinke: Thermodynamic properties of the elements, *Advan. Chem. Ser.*, no. 18, 1956,

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We hope this is concerned with the metallurgy of zinc. The only other uses of ZnO are presented below.

ACKNOWLEDGMENTS

The authors are pleased to acknowledge the following contributions by members of the Metallurgical Branch Staff: J. R. Rossini, K. K. Kelley, R. H. Bernhardt, cooperation of bellows-gasometer; R. A. Charleton, operation of equipment; R. H. Lake, differential thermal analysis; P. W. Plummer, thermogravimetric analysis; and M. E. V. Plummer, preparation of ZnO · 3ZnS, sample.

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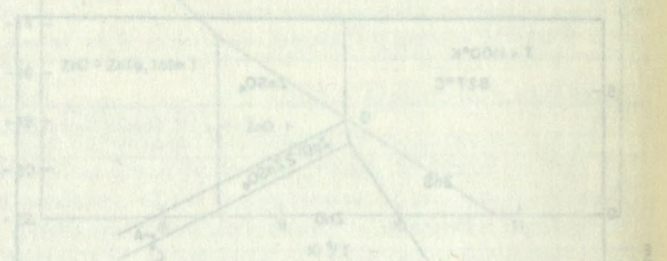


Fig. 4. The graph shows the relationship between temperature and composition for ZnO-ZnS. The x-axis represents the mole fraction of ZnS, and the y-axis represents temperature in degrees Celsius. Key points are marked: 827°C at 100% ZnS, 1100°C at approximately 20% ZnS, and 1200°C at 0% ZnS.

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